Chapter 15. Chemical Equilibrium

15.1 The Concept of Equilibrium

• Consider colorless frozen N\textsubscript{2}O\textsubscript{4}.
  • At room temperature, it decomposes to brown NO\textsubscript{2}.
    \[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]
  • At some time, the color stops changing and we have a mixture of N\textsubscript{2}O\textsubscript{4} and NO\textsubscript{2}.
  • **Chemical equilibrium** is the point at which the concentrations of all species are constant.
    • Opposing reactions proceed at equal rates.
  • Assume that both the forward and reverse reactions are elementary processes.
  • We can write rate expressions for each reaction.
    • **Forward reaction:** \( \text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g) \)
      \[ \text{Rate}_f = k_f[N_2O_4] \]
      \[ k_f = \text{rate constant (forward reaction)} \]
    • **Reverse reaction:** \( 2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \)
      \[ \text{Rate}_r = k_r[\text{NO}_2]^2 \]
      \[ k_r = \text{rate constant (reverse reaction)} \]
  • Place some pure N\textsubscript{2}O\textsubscript{4} into a closed container.
    • As N\textsubscript{2}O\textsubscript{4} reacts to form NO\textsubscript{2}, the concentration of N\textsubscript{2}O\textsubscript{4} will decrease and the concentration of NO\textsubscript{2} will increase.
    • Thus, we expect the forward reaction rate to slow and the reverse reaction rate to increase.
    • Eventually we get to equilibrium where the forward and reverse rates are equal.
    • At equilibrium:
      \[ k_f[N_2O_4] = k_r[\text{NO}_2]^2 \]
    • Rearranging, we get:
      \[ k_f/k_r = \text{a constant} \]
    • At equilibrium the concentrations of N\textsubscript{2}O\textsubscript{4} and NO\textsubscript{2} do not change.
    • This mixture is called an **equilibrium mixture**.
    • The equilibrium mixture results because the reaction is reversible.
    • This is an example of a dynamic equilibrium.
    • A dynamic equilibrium exists when the rates of the forward and reverse reactions are equal.
    • No further net change in reactant or product concentration occurs.
    • The double arrow \( \rightleftharpoons \) implies that the process is dynamic.

15.2 The Equilibrium Constant

• Consider the **Haber process**:
  \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
• It is used for the preparation of ammonia from nitrogen and hydrogen.
• The process is carried out at high temperature and pressure.
  • Ammonia is a good source of fixed nitrogen for plants.
  • Much of the NH\textsubscript{3} produced industrially is used as a fertilizer.
• If we start with a mixture of nitrogen and hydrogen (in any proportions), the reaction will reach equilibrium with constant concentrations of nitrogen, hydrogen, and ammonia.
• However, if we start with just ammonia and no nitrogen or hydrogen, the reaction will proceed and N\textsubscript{2} and H\textsubscript{2} will be produced until equilibrium is achieved.
• No matter what the starting composition of reactants and products is, the equilibrium mixture contains the same relative concentrations of reactants and products.
• Equilibrium can be reached from either direction.
• We can write an expression for the relationship between the concentration of the reactants and products at equilibrium.
  • This expression is based on the **law of mass action**.
  • For a general reaction,
    \[ a\text{A} + b\text{B} \rightleftharpoons d\text{D} + e\text{E} \]
  • The **equilibrium-constant expression** is given by:
    \[ K_c = \frac{[\text{D}^d][\text{E}]^e}{[\text{A}]^a[\text{B}]^b} \]
- Where $K_c$ is the **equilibrium constant**.
- The subscript “c” indicates that molar concentrations were used to evaluate the constant.
- Note that the equilibrium constant expression has products in the numerator and reactants in the denominator.

**Evaluating $K_c$**
- The value of $K_c$ does not depend on initial concentrations of products or reactants.
  - Consider the reaction: \[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]
  - The equilibrium constant is given by: \[ K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \]
  - The value of this constant (at 100 °C) is 6.50 (regardless of the initial concentrations of N$_2$O$_4$(g) or NO$_2$(g)).
- The equilibrium expression depends on stoichiometry.
  - It does not depend on the reaction mechanism.
  - The value of $K_c$ varies with temperature.
- We generally omit the units of the equilibrium constant.

**Equilibrium Constants in Terms of Pressure, $K_p$**
- When the reactants and products are gases, we can write an equilibrium expression using partial pressures rather than molar concentrations.
  - The equilibrium constant is $K_p$ where “p” stands for pressure.
  - For the reaction: \[ aA + bB \rightleftharpoons dD + eE \]
    \[ K_p = \frac{(P_D)^d (P_E)^e}{(P_A)^a (P_B)^b} \]
  - They can be interconverted using the ideal gas equation and our definition of molarity: $PV = nRT$ thus $P = (n/V)RT$.
  - If we express volume in liters the quantity $(n/V)$ is equivalent to molarity.
  - Thus the partial pressure of a substance, A, is given as: $P_A = (n/V)RT = [A]RT$.
- We can use this to obtain a general expression relating $K_c$ and $K_p$: $K_p = K_c(RT)^{\Delta n}$.
  - Where $\Delta n$ = (moles of gaseous products) – (moles of gaseous reactants).
  - The numerical values of $K_c$ and $K_p$ will differ if $\Delta n = 0$.

**Equilibrium Constants and Units**
- Equilibrium constants are reported without units.
  - The equilibrium constant may be derived from thermodynamic measurements.
  - The constants are defined in terms of activities rather than concentrations or partial pressures.
  - The activity of a substance in an *ideal* mixture is the ratio of the concentration or pressure of the substance either to a reference concentration (1 $M$) or a reference pressure (1 atm).
    - The units in these ratios cancel, thus activities have no units.
    - The numerical value of the activity equals the concentration.
    - For pure solids and pure liquids, the activities equal 1.
  - What about “real” systems?
    - Here activities also have no units.
    - The activities are not exactly equal to concentration but we will ignore the differences.
    - *Thermodynamic equilibrium constants* derived from these activities also have no units.
15.3 Understanding and Working with Equilibrium Constants

The Magnitude of Equilibrium Constants
- The equilibrium constant, $K$, is the ratio of products to reactants.
  - Therefore, the larger $K$ the more products are present at equilibrium.
  - Conversely, the smaller $K$ the more reactants are present at equilibrium.
    - If $K \gg 1$, then products dominate at equilibrium and equilibrium lies to the right.
    - If $K \ll 1$, then reactants dominate at equilibrium and the equilibrium lies to the left.

The Direction of the Chemical Equation and $K$
- An equilibrium can be approached from either direction.
- Consider the reaction:
  \[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]
  - The equilibrium constant for this reaction (at 100 °C) is:
    \[ K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \]
  - However, when we write the equilibrium expression for the reverse reaction,
    \[ 2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]
  - The equilibrium constant for this reaction (at 100 °C) is:
    \[ K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = 4.72 \]
- The equilibrium constant for a reaction in one direction is the reciprocal of the equilibrium constant of the reaction in the reverse direction.

Relating Chemical Equation Stoichiometry and Equilibrium Constants
- It is possible to calculate the equilibrium constant for a reaction if we know the equilibrium constants for other reactions that add up to give us the one we want.
  - This is similar to using Hess’s law.
    - The equilibrium constant of a reaction in the reverse direction is the inverse of the equilibrium constant of the reaction in the forward direction.
    - The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power equal to that number.
    - The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

15.4 Heterogeneous Equilibria
- Equilibria in which all reactants and products are present in the same phase are called homogeneous equilibria.
- Equilibria in which one or more reactants or products are present in a different phase are called heterogeneous equilibria.
- Consider the equilibrium established when solid lead(II) chloride dissolves in water to form a saturated solution:
  \[ \text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \]
  - Experimentally, the amount of Pb$^{2+}$ and Cl$^-$ does not depend on the amount of PbCl$_2$.
  - Why?
  - The concentration of a pure solid or pure liquid equals its density divided by its molar mass.
  - Neither density nor molar mass is a variable.
  - Thus the concentrations of solids and pure liquids are constant.
  - For the dissolution of PbCl$_2$:
    \[ K_c = [\text{Pb}^{2+}][\text{Cl}^-]^2 \]
  - If a pure solid or pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium constant expression.
• Note: Although the concentrations of these species are not included in the equilibrium expression, they do participate in the reaction and must be present for an equilibrium to be established!

• Other common examples of heterogeneous equilibria include:
  - systems involving solids and gases.
    - Example: CaCO$_3$(s) $\rightleftharpoons$ CaO(s) + CO$_2$(g)
      $$K_c = [CO_2] \text{ and } K_p = P_{CO_2}$$
  - systems where the solvent is involved as a reactant or product and the solutes are present at low concentrations.
    - Example: H$_2$O(l) + CO$_3^{2-}$(aq) $\rightleftharpoons$ OH$^-$ (aq) + HCO$_3^-$ (aq)
      $$K_c = [OH^-][HCO_3^-] / [CO_3^{2-}]$$
      - Here the concentration of water is essentially constant and we can think of it as a pure liquid.

### 15.5 Calculating Equilibrium Constants

• Proceed as follows:
  - Tabulate initial and equilibrium concentrations (or partial pressures) for all species in the equilibrium.
  - If an initial and an equilibrium concentration are given for a species, calculate the change in concentration.
  - Use the coefficients in the balanced chemical equation to calculate the changes in concentration of all species.
  - Deduce the equilibrium concentrations of all species.
  - Use these to calculate the value of the equilibrium constant.

### 15.6 Applications of Equilibrium Constants

#### Predicting the Direction of Reaction

- For a general reaction: $aA + bB \rightleftharpoons dD + eE$
- We define $Q$, the reaction quotient, as:
  $$Q = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$
- Where [A], [B], [D], and [E] are molarities (for substances in solution) or partial pressures (for gases) at any given time.
- We can compare $Q_c$ to $K_c$ or $Q_p$ to $K_p$:
  - If $Q = K$, then the system is at equilibrium.
  - If $Q < K$, then the forward reaction must occur to reach equilibrium.
  - If $Q > K$, then the reverse reaction must occur to reach equilibrium.
    - Products are consumed, reactants are formed.
    - $Q$ decreases until it equals $K$.

#### Calculating Equilibrium Concentrations

- The same steps used to calculate equilibrium constants are used to calculate equilibrium concentrations.
- Generally, we do not have a number for the change in concentration.
- Therefore, we need to assume that $x$ mol/L of a species is produced (or used).
- The equilibrium concentrations are given as algebraic expressions.

### 15.7 Le Châtelier’s Principle

- Consider the Haber process: 
  $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
  - As the pressure increases, the amount of ammonia present at equilibrium increases.
  - As the temperature increases, the amount of ammonia at equilibrium decreases.
  - Can this be predicted?
• Yes! We can use Le Châtelier’s principle to make qualitative predictions about how a system at equilibrium responds to various changes in external conditions.
• Le Châtelier’s principle: if a system at equilibrium is disturbed by a change in temperature, a change in pressure, or a change in the concentration of one or more components, the system will shift its equilibrium position in such a way as to counteract the effects of the disturbance.

**Change in Reactant or Product Concentration**

- If a chemical system is at equilibrium and we add or remove a product or reactant, the reaction will shift so as to reestablish equilibrium.
- For example, consider the Haber process again:
  \[ \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \]
- If \( \text{H}_2 \) is added while the system is at equilibrium, \( Q < K \).
  • The system must respond to counteract the added \( \text{H}_2 \) (Le Châtelier’s principle).
  • That is, the system must consume the \( \text{H}_2 \) and produce products until a new equilibrium is established.
  • Therefore, \([\text{H}_2]\) and \([\text{N}_2]\) will decrease and \([\text{NH}_3]\) will increase until \( Q = K \).
- We can exploit this industrially.
  • Suppose that we wanted to optimize the amount of ammonia we formed from the Haber process.
  • We might flood the reaction vessel with reactants and continuously remove product.
  • The amount of ammonia produced is optimized because the product (\( \text{NH}_3 \)) is continuously removed and the reactants (\( \text{N}_2 \) and \( \text{H}_2 \)) are continuously being added.

**Effects of Volume and Pressure Changes**

- Consider a system at equilibrium.
- If the equilibrium involves gaseous products or reactants, the concentration of these species will be changed if we change the volume of the container.
  • For example, if we decrease the volume of the container, the partial pressures of each gaseous species will increase.
  • Le Châtelier’s principle predicts that if pressure is increased, the system will shift to counteract the increase.
  • That is, the system shifts to remove gases and decrease pressure.
  • An increase in pressure favors the direction that has fewer moles of gas.
- Consider the following system:
  \[ \text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \]
  • An increase in pressure (by decreasing the volume) favors the formation of colorless \( \text{N}_2\text{O}_4 \).
  • The instant the pressure increases, the concentration of both gases increases and the system is not at equilibrium.
  • The system changes to reduce the number moles of gas.
  • A new equilibrium is established.
  • The mixture is lighter in color.
  • Some of the brown \( \text{NO}_2 \) has been converted into colorless \( \text{N}_2\text{O}_4(\text{g}) \)
- In a reaction with the same number of moles of gas in the products and reactants, changing the pressure has no effect on the equilibrium.
- In addition, no change will occur if we increase the total gas pressure by the addition of a gas that is not involved in the reaction.

**Effect of Temperature Changes**

- The equilibrium constant is temperature dependent.
- How will a change in temperature alter a system at equilibrium?
  • It depends on the particular reaction.
  • For example, consider the endothermic reaction:
    \[ \text{Co(H}_2\text{O)}_6^{2+}(aq) + 4\text{Cl}^-(aq) \rightleftharpoons \text{CoCl}_4^{2-}(aq) + 6\text{H}_2\text{O(l)} \quad \Delta H > 0 \]
  • \( \text{Co(H}_2\text{O)}_6^{2+} \) is pale pink and \( \text{CoCl}_4^{2-} \) is a deep blue.
  • At room temperature, an equilibrium mixture (light purple) is placed in a beaker of warm water.
    • The mixture turns deep blue.
• This indicates a shift toward products (blue \( \text{CoCl}_4^{2-} \)).
• This reaction is endothermic.
• For an endothermic reaction (\( \Delta H > 0 \)), heat can be considered as a reactant.
  • Thus, adding heat causes a shift in the forward direction.
• The room-temperature equilibrium mixture is placed in a beaker of ice water.
  • The mixture turns bright pink.
  • This indicates a shift toward reactants (pink \( \text{Co(H}_2\text{O)}_6^{2+} \)).
  • In this case, by cooling the system we are removing a reactant (heat).
  • Thus, the reaction is shifted in the reverse reaction.
• A change in temperature causes a change in the value of \( K \).
  • If we increase the temperature of an endothermic reaction, \( K \) increases.
  • If we increase the temperature of an exothermic reaction, \( K \) decreases.

The Effect of Catalysts
• A catalyst lowers the activation energy barrier for the reaction.
  • Therefore, a catalyst will decrease the amount of time needed to reach equilibrium.
  • A catalyst does not affect the composition of the equilibrium mixture.

Selected Problems: 14, 15, 21, 23, 25, 27, 32, 33, 35, 37, 38, 39, 40, 45, 46, 49, 50, 51, 53, 57, 59, 60, 61, 62, 63.